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Self assembly of magnetically interacting cubes by a turbulent fluid flow

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Previous work (e.g. [1], [2]) has demonstrated that combining mechanical vibration with magnetic interactions can result in the self assembly of complex structures, albeit at low yield. Here we introduce a system where the yield of self assembled structures is quantitatively predicted by a theoretical analysis. Millimeter sized magnetic blocks, designed to form chains as their minimal energy state, are placed in a turbulent fluid flow. The distribution of chain lengths that form is quantitatively consistent with predictions, showing that the chain length distribution coincides with that of monomers/polymers in a thermal bath, with the turbulence strength parameterizing the effective temperature.

Self assembly promises a new paradigm for manufacturing small devices: instead of piece-by-piece manufacturing, structures could spontaneously assemble from individual components into functional devices [1, 3–6]. Enabling this technology requires understanding how to design parts, and protocols for their assembly, such that structures assemble with high yield. Examples from physics have abundantly shown that collections of identical parts, under either equilibrium [7, 8] or nonequilibrium conditions[9], allow many different structures to form, each in low yield. The fundamental question is to understand how to choose the parts, component and the recipe for self-assembly, to maximize the yield of a pre-specified product. To date, perhaps the most versatile strategy for self-assembly that has been employed uses DNA [10, 11]. This work includes the demonstrations of DNA assembly of complex two dimensional shapes [10] and non-trivial dynamic structures such as an autonomous walker [11, 12].

DNA-based self-assembly brings great variability to the generation of molecular assemblies with unexpectedly complex geometries, but has not, so far, suggested strategies for assembly of functional structures. Practical materials require the development of methods for assembling structures other than DNA, or those based on DNA at length scales ranging from microscopic to macroscopic. Whereas submicron assembly can be driven by thermal fluctuations, macroscopic (i.e. \sim mm sized) assembly cannot; in this range of sizes, assembly requires inputting energy. A common method for assembling macroscopic objects is vibration. For example Boncheva *et. al.* [1] showed that shaking a PDMS sheet embedded with small magnets allowed the sheet to fold into a closed structure; Rothmund showed that shaking floating particles [2], with hydrophobic and hydrophilic patches, could facilitate the formation of dense prespecified arrays. But in both cases, the dynamics leads to structures that do not have the desired pattern; for example, the yield for folding sheets into closed surfaces is in practice quite small; others, such as Jacobs *et al.* [13] report high-yield self-assembled structures based on capillary interactions in low melting temperature solders.

For vibration-based self assembly to be a viable manufacturing strategy, we must design structures and strategies for agitation that will allow self assembly to proceed to a desired state in high yield. The first step in developing a design strategy is the ability to predict yield quantitatively. With an accurate quantitative model for yield, we can design systems (component parts and vibration strategy) where the yield is maximized. Heretofore, studies of vibration-based self assembly have been qualitative, with no underlying theoretical basis.

The goal of this Letter is therefore to introduce a system in which the self assembly yield can be quantitatively controlled and compared with theoretical predictions. To this end, we have designed a system, in which millimeter sized magnetic blocks assemble into chains in a turbulent fluid flow. The statistics of turbulent fluid flows have been well characterized [14–16], leading to a stochastic forcing of the particles; this is precisely analogous to a thermal bath, with the effective temperature depending on the strength of the turbulence. The distribution of chain lengths of the magnetic blocks can be controlled either by changing the strength of the turbulence or the magnetic binding energy. The observed distributions are well described by a theoretical model, which is based on a first-principles description of the mechanics of particles in a turbulent flow.

The magnetic blocks are polydimethylsiloxane (PDMS) cubes (side length 1 cm), with small disc-shaped magnets (1/8" diameter and 1/32" thickness, made out of NdFeB) embedded in the center of one face of the cube, with the north pole facing outwards. A $1/4" \times 1/4" \times 1/8"$ square prism of soft ferromagnetic NiCu alloy is embedded on the opposite face. (Figure 1a) Two such cubes interact by lining up the permanent magnet with NiCu; all other permutations are not energetically favorable, since two faces with identical magnets repel, and there is no significant interaction between two faces with NiCu. The NiCu was selected because of its easily accessible Curie temperature, or the temperature where the material turns from ferromagnetic to paramagnetic. We measured the low Curie temperature for this alloy to be $T_{curie} = 165^\circ\text{C}$; this

value of T_{curie} is such that we can tune the interaction energy between the magnets by changing the temperature of the system. To tune the vibrations, we place N cubes in a closed container (diameter 8 cm and height 10 cm) filled with water with 0.3 M CsCl (for matching the density of the cubes) and 10 mM Triton-X 100 (to minimize bubble formation on agitation). The jar is then attached to a 60 cm diameter disc which is rotated at a frequency f between 9 rpm and 80 rpm (Figure 1b). Changing the rotation frequency allows a continuous tuning of the strength of the turbulence.

In a typical experiment, we begin with $N = 12$ dissociated monomers, and rotate the jar for 50 full rotations. We then examine the distributions of chain lengths that form (Figure 1c). The chains are manually disassembled into monomers before repeating the experiment. Figure 2a shows the results of the experiment at room temperature. For each rotation frequency f , a range of different chain lengths can form, though there is a chain length N^* for which the yield is maximal. N^* decreases with increasing f . The distribution is broad peaked, so that the yield at the maximum N is rather low, of order 15–20%. By changing the temperature to $T = 80^\circ\text{C}$, we can tune the strength of the magnetic interaction, and hence shift the distribution (Fig. 2b)

We now turn to a theoretical description of the assembly process. The rotation of the cylinder produces a time-dependent flow inside the jar; the monomers move both from their interactions with each other and from the turbulence. The translational equation of motion for the center of mass of the i -th monomer is thus

$$m_p \frac{d^2 x_i}{dt^2} = c_D \frac{dx_i}{dt} - \nabla V(X_i) + \xi(t) \quad (1)$$

The inertia of the particle, with mass m_p , is dissipated in proportion to the velocity of the particle, where c_D is the drag coefficient. The particles interact with each other through a magnetic potential, $V(x_i) = \sum_{i \neq j} U(|x_i - x_j|)$, which sums the magnetic interaction ($U(\eta)$) set up by the surrounding particles. $\xi(t)$ represents the agitation the flow provides to the particle.

The quantitative values of both the drag coefficient c_D and the turbulent forcing $\xi(t)$ depends on the relative size of the particles to the turbulent eddies in the fluid flow. A typical eddy size is the Kolmogorov microscale, ℓ_η , the lengthscale at which the local Reynolds number is equal to unity; in the present experiments, this is $\ell_\eta \approx 10^{-3}\text{cm}$, far smaller than the size of the cube, $d_p \approx 1\text{cm}$. This implies that the drag on the particle is dominated by the viscous stresses exerted on the particles by the eddies of competing size. Phenomenological characterizations of this drag [17] estimate the drag coefficient to be $c_D = 24\pi\mu d_p(1 + 0.1315Re_p^n)$, where $Re_p = (d_p/\ell_\eta)^{4/3}$ and $n = 0.82 - 0.05\log_{10}Re_p$.

To understand the turbulent forcing $\xi(t)$, note that the typical deceleration timescale for the particle (m_p/c_D) is

≈ 25 times slower than the turnover timescale of turbulent eddies [14, 17]. Thus, on the typical time scales of particle motion, the fluid forcing behaves as a time-uncorrelated process [18–20]. The central limit theorem therefore implies that the fluid forcing is temporally uncorrelated, Gaussian, with zero mean. Hence we have $\langle \xi(t) \rangle = 0$ and $\langle \xi(t')\xi(t'') \rangle = 2q\delta(t' - t'')$, which implies a particle diffusion constant to be $D = m^2q/2c_D^2$. The noise strength q can be estimated by considering that the viscous stress exerted by an eddy of size d_p on the particle is $\tau \sim \mu\langle \delta u(d_p)^2 \rangle^{1/2}/d_p$, where $\langle \delta u(d_p)^2 \rangle^{1/2}$, is the typical velocity of an eddy of size d_p . This quantity is referred to as the second order structure function of a turbulent flow and several investigators [16] have confirmed the scaling laws predicted by Kolmogorov's theory. We can hence estimate $q \approx 0.147(\text{cm/s}^2)^2$ and $c_D/m \approx 5\text{sec}^{-1}$ for the current system.

With these assumptions, Eqn. 1 is a classical Langevin equation [21]. The flow configuration is therefore identical to a set of interacting particles in a thermal bath, with an effective temperature $k_B T_{eff} = c_D D$. The stationary probability distribution can be obtained by solving the associated Fokker-Planck equation; this stationary distribution is simply given by the Boltzmann distribution for the interacting particles, with the temperature T_{eff} . The present problem is analogous to finding the probability distribution of the distribution P_N of chain lengths of linear monomers of length N in a thermal bath, a classical problem of polymer physics [22]. The probability distribution requires computing the partition function $\sum_N Q_N$, for linear aggregates of size N ; this decomposes into its translation (q_t), rotational (q_r), vibrational (q_v) and bulk terms

$$Q_N = q_t^{(N)} q_r^{(N)} (q_v e^{-V^*/k_B T_{eff}})^N, \quad (2)$$

where V^* is the binding energy of two magnets to each other.

Following [22], we can evaluate the various partition functions: the translational partition function $q_t \sim (Nm k_B T_{eff})^{3/2}$, whereas the rotational partition function for a rod of length $L = N\ell$, where ℓ is the dimension of each block, is given by $q_r \sim (I_{AN} k_B T_{eff})^{1/2} (I_{BN} k_B T_{eff})$, where I_{AN}, I_{BN} are the moment of inertia for rotating a linear aggregate of length N around its long axis and perpendicular axes, respectively. These are thus given by $I_{AN} = m\ell^2 N/8$ and $I_{BN} \approx mNL^2/48 = mN^3\ell^2/48$, respectively. Putting this together we have that $Q_N \sim N^5 x^N$, where the factor $x = e^{-V^*/k_B T_{eff}}$. This therefore implies that the probability distribution is given by

$$\frac{P}{P_{N_m}} = \left[\frac{N}{N_m} \exp\left(1 - \frac{N}{N_m}\right) \right]^5, \quad (3)$$

where the most probable configuration occurs at chain

length N_m

$$N_m \sim -\frac{5k_B T_{eff}}{V^*} \quad (4)$$

This theoretical description makes a number of explicit predictions that can be tested in experiments. First, the shape of the probability distribution depends on a single parameter N_m ; if we take the measured distributions shown in Fig. 2 and rescale the chain lengths by N_m , and rescale the probabilities by the measured $P(N_m)$ the distributions should collapse onto a single curve. Figure 3 shows this collapse, compared with the theoretical prediction for the shape of the distribution given in Eqn. 3. The different colors in the figure represent different rotation speeds, whereas the different symbol shapes represent two different temperatures (magnetic binding strengths). The error bars on the data points correspond to statistical sampling error [23].

A second prediction of the theory is that the peak position N_m should decrease linearly with the angular velocity of the rotation and depends inversely on the magnetic interaction energy V^* between the monomers. The experiments reported in Fig. 2 vary both f and V^* ; changing the temperature from 21°C to 80°C roughly halves V^* . Figure 4 confirms both predicted relationships, the linear dependence on ω and the predicted change in this relationship following an increase in the real temperature.

To summarize, we have demonstrated that a turbulent flow can be used to create a well controlled effective thermal bath for a mesoscopic self assembling system. This allows the design of an experimental system where the assembly yield can be well controlled, and predicted by theoretical analysis. Changing both the strength of the turbulence and the binding energy of the magnets causes changes in the measured probability distributions of the chain lengths that are well captured by the theory. While the theory explained here predicts well the behavior of the system, it should be noted that Eqn. 3 is valid in the dilute limit; further refinements, such as hydrodynamic effects between cubes, have been ignored since these effects are smaller than the magnetic interactions between the cubes when in close proximity to each other.

This work leads to several points that are significant for meso-scale self-assembly: The ability to create a controlled white noise source where the assembled yield can be predicted leads to the possibility of *a priori* designing the interactions between the structures (by tuning the strengths of the magnets or their positions) to maximize the yield of the desired structure. More generally, there is tremendous opportunity for using flow fields – turbulent or not – for controlling the assembly of mesoscopic objects. While this idea is in its infancy, the simple method seems to present opportunity for controlling and designing self-assembling system on intermediate length scales. Another intriguing possibility is the use of chaotic advection in planar or microfluidic flows for creating effective

temperature fields for millimeter-sized objects. The advantage here is that in addition to the random component there is also a mean flow; one could imagine creating a multi-staged “factory” for creating complex structures. A major challenge is to use this methodology to design useful structures at the millimeter scale, where the flow characteristics and interactions are chosen to maximize yield.

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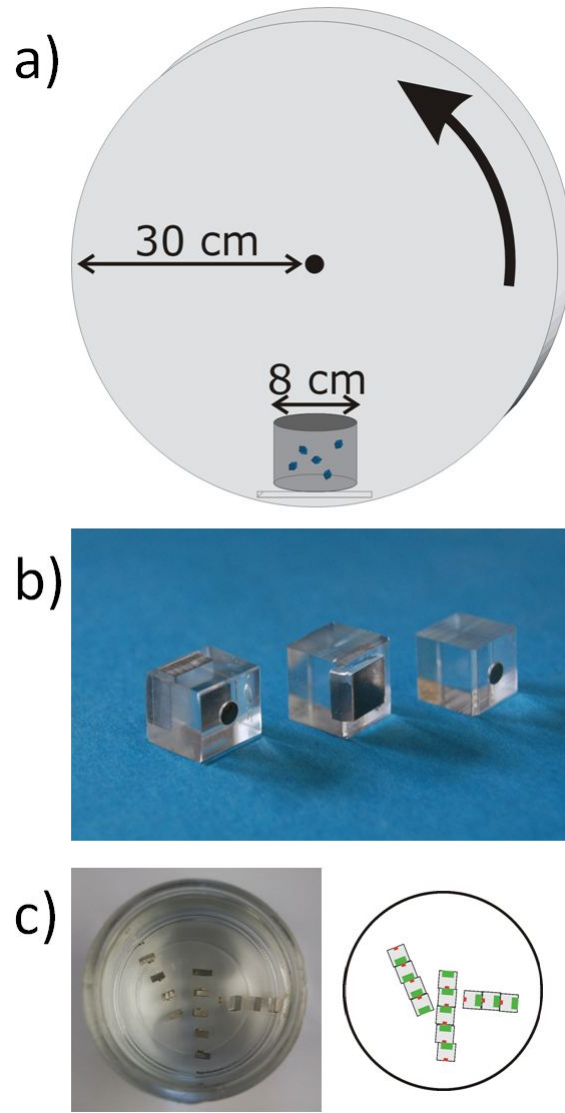


FIG. 1. (a) Schematic sketch of the experiment. N cubes are placed in a closed container, which is then attached to a rotating disk that generates a turbulent flow. (b) Polydimethylsiloxane blocks with small embedded disk shape magnets and prism-shaped NiCu pieces. (c) Agitation in a turbulent flow causes the blocks to form chains; green are the NiCu pieces and red are the magnets.

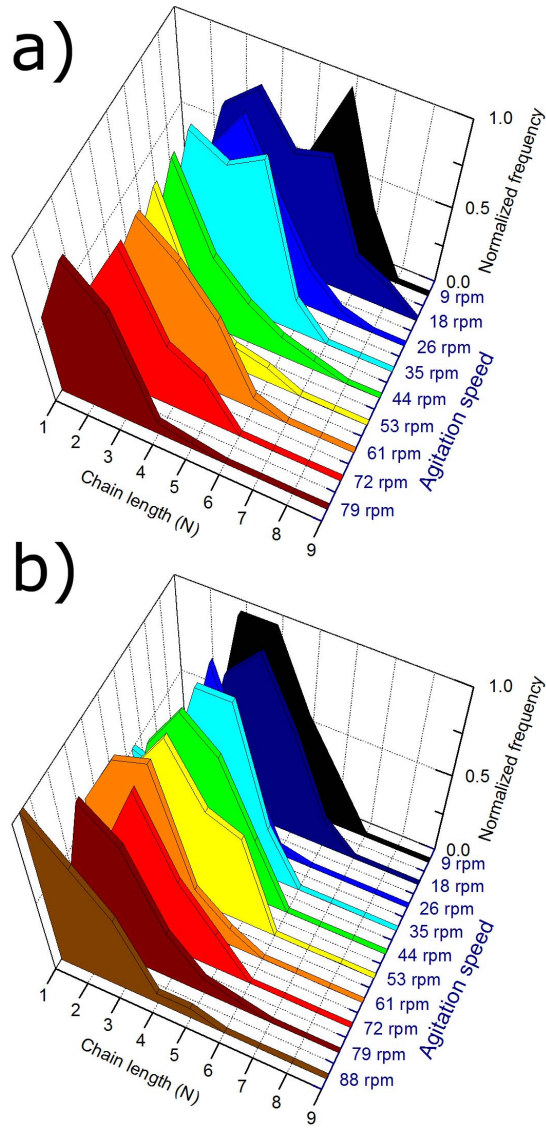


FIG. 2. Histogram of the distribution of chain lengths measured in the experiment, for a range of different rotation rates, and both (a) room temperature and (b) $T = 80^\circ\text{C}$. Changing the temperature shifts the strength of the magnetic interaction. The peak of the distribution shifts as a function of both temperature and rotation rate.

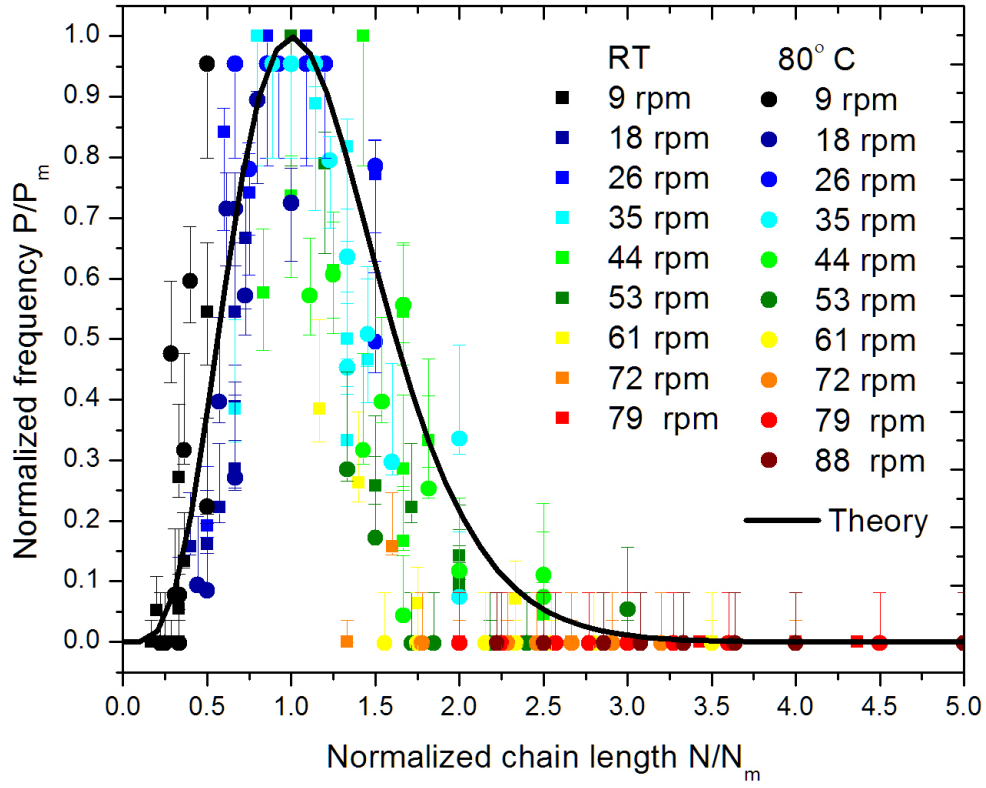


FIG. 3. Comparison of theoretical prediction and normalized experimental results: symbols represent data from aggregates at room temperature and 80°C, the colors represent different rotation speeds. The solid line is the theoretical prediction (Eqn. 3). The error bars are statistical [23].

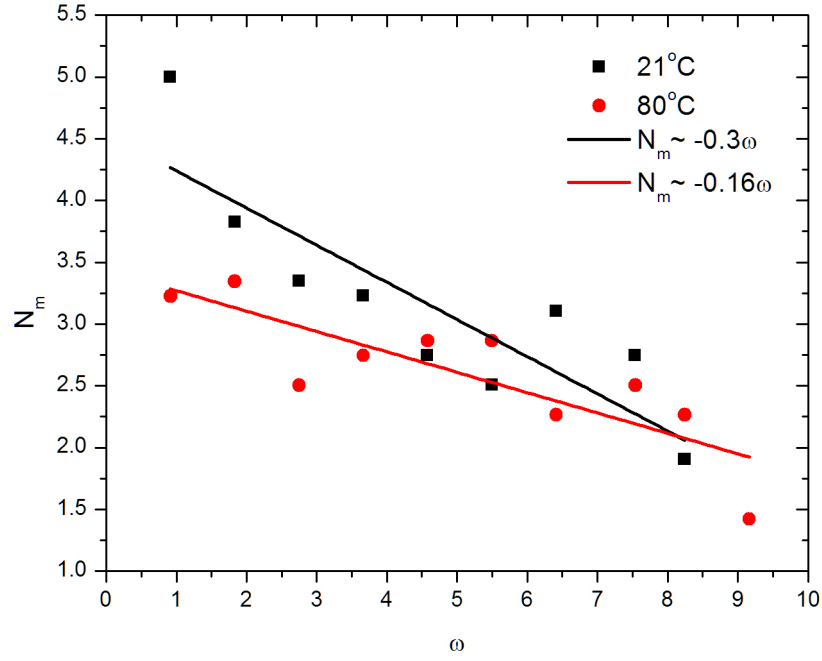


FIG. 4. Peak position, N_m , versus the angular velocity of the jar, ω : circles represent data from experiments conducted at room-temperature and 80°C . — is a best fit line through the data with the gradient stated in the legend. This provides evidence for the predicted linear relationship between N_m and ω and the dependence on the interaction energy.